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Note

Synthesis of 2-acetamido-1,2-dideoxy-D-*galacto*-nojirimycin (2-acetamido-1,2,5-trideoxy-1,5-imino-D-galactitol) from 1-deoxynojirimycin*

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Several routes to ring-aza analogues of 2-acetamido-1,5-anhydro-2-deoxyhexitols have been reported[2]. However, the synthesis of 2-acetamido-1,2,5-trideoxy-1,5-imino-D-galactitol (**1**) from 1-deoxynojirimycin has not been reported hitherto and a synthesis is now described.

Hydrogenolysis of *N*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-mannitol (**2**), readily obtained from 1-deoxynojirimycin, gave synthon **3** which was converted into the *N*-benzyloxycarbonyl derivative **4** (90%). Treatment of **4** with thionyl chloride in ethyl acetate–triethylamine at 0° gave a mixture of the diastereomers of the cyclic sulphite **5**. Treatment of **5** with lithium azide in *N,N*-dimethylformamide at 90° and chromatography of the products gave 52% of the 2-azido D-*gluco* compound **6** and 4% of the 3-azido D-*talo* isomer **7**. Reaction of **6** with benzyl bromide and potassium hydroxide in tetrahydrofuran gave the 3-*O*-benzyl derivative **8**, and hydrolysis (pH 3) gave the diol **9**. Treatment of **9** with potassium carbonate in aqueous *N,N*-dimethylformamide gave the crystalline cyclic carbamate **10**. Reaction of the 4-mesylate (**11**) of **10** with lithium benzoate in anhydrous *N,N*-dimethylformamide gave the D-*galacto* benzoate **12** (>90%). Saponification of **12** with aqueous sodium hydroxide in dichloromethane–methanol yielded the alcohol **13** which, in boiling methanolic barium hydroxide, gave ~80% of **14**. Hydrogenolysis (Pd–C) of **14** in acetic anhydride gave crude **1**, which was acetylated, purified by chromatography, and deacetylated with methanolic sodium methoxide to give 62% of the crystalline target compound **1**.

The introduction of the azido group by cleavage of the cyclic sulphite in **5** is the key step in the above synthesis of **1**. The yield (56%) of **6** was not optimized, but the introduction of an equatorial 2-azide group clearly preponderates. The "regioselective excess" (r.e.) of the reaction was 85%, which demonstrates the value of the cyclic

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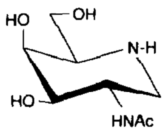
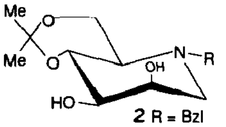
* The Chemistry of the 1-Deoxynojirimycin System, Part III. For Part II, see ref. 1.



1



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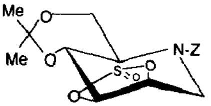
4 R = Z



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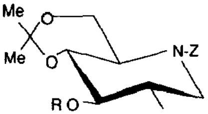

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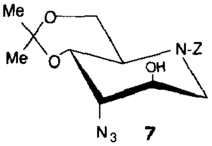
8 R = Bzl



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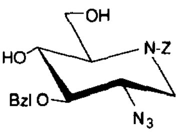

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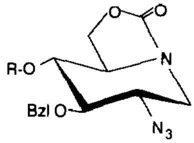

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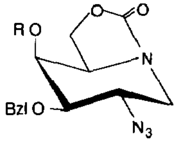

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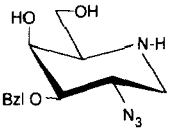
13 R = H



14

sulphite group, considering that the reaction can be performed easily on a large preparative scale.

EXPERIMENTAL

General. — See preceding Note[1].

*1,5-Dideoxy-1,5-imino-4,6-*O*-isopropylidene-*D*-mannitol acetate* (**3**). — A solution of **2** (ref. 2) (72.5 g, 0.25 mol) in methanol (250 mL) and glacial acetic acid (17 mL) was stirred for 5 h at 40° under hydrogen at 0.3 MPa in the presence of 10% Pd–C (10 g), then filtered, and concentrated. The crystalline product (65.8 g, 99%) had m.p. 159°, $[\alpha]_D^{20}$ −52.5° (c 1.1, chloroform): ^{1}H-N.m.r. data (CD_3OD): δ 1.37, 1.51, 1.95 (3 s, 9 H, 3 CMe), 2.63 (ddd, 1 H, $J_{4,5}$ 8.0, $J_{5,6a}$ = $J_{5,6b}$ = 10.0 Hz, H-5), 2.96 (dd, 1 H, $J_{1a,1b}$ 13.5, $J_{1a,2}$ 1.3 Hz, H-1a), 3.11 (dd, 1 H, $J_{1b,2}$ 2.6 Hz, H-1b), 3.55 (dd, 1 H, $J_{3,2}$ 3.0, $J_{3,4}$ 9.5 Hz, H-3), 3.79 (d, 2 H, H-6a,6b), and 3.93–3.99 (m, 2 H, H-2,4).

Anal. Calc. for $C_{11}H_{21}NO_6$: C, 50.2; H, 8.0; N, 5.3. Found: C, 50.9; H, 7.9; N, 5.4.

N-*Benzyloxycarbonyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-*D*-mannitol* (**4**). — To a solution of **3** (108.6 g, 0.53 mol) in *N,N*-dimethylformamide (1.5 L) in which was suspended K_2CO_3 (86.9 g, 0.63 mol), benzyl chloroformate (99.5 g, 0.58 mol) was added dropwise at 0°. After 30 min, the evolution of gas ceased and t.l.c. (5:1 toluene–ethanol) revealed only **4** (R_F 0.35). The mixture was filtered, the insoluble material was washed twice with *N,N*-dimethylformamide (200 mL), and the combined filtrate and washings were concentrated. A solution of the residue in chloroform was washed twice with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated. The residue crystallized from ethyl acetate to give **4** (155.6 g, 0.64 mol, 87%), m.p. 79–81°, $[\alpha]_D^{20}$ −8° (*c* 1, chloroform). ^{1}H-N.m.r. data (CDCl$_3$): δ 1.41, 1.52 (2 s, 6 H, CMe$_2$), 2.58, 2.75 (2 bs, 2 H, 2 OH), 2.92 (bd, 1 H, $J_{5,6a}$ 5.0, $J_{5,6b}$ 11.2 Hz, H-5), 3.57 (bddd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 9.9, $J_{3,OH}$ 2.0 Hz, H-3), 3.99 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.02 (bs, 1 H, H-2), 4.31 (dd, 1 H, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.44 (dd, 1 H, $J_{1b,2}$ 3.1 Hz, H-1b), 4.64 (dd, 1 H, H-6b), 5.05–5.14 (2 d, 2 H, J_{AB} 12.6 Hz, PhC*H*$_2$), and 7.28–7.43 (m, 5 H, Ph).

Anal. Calc. for $C_{17}H_{23}NO_6$: C, 60.4; H, 6.9; N, 4.1. Found: C, 61.1; H, 7.1; N, 3.8.

*2-Azido-*N*-benzyloxycarbonyl-1,2,5-trideoxy-1,5-imino-4,6-*O*-isopropylidene-*D*-glucitol* (**6**). — To a solution of **4** (34.3 g, 102 mmol) in ethyl acetate (350 mL) and triethylamine (22.3 g, 0.220 mol) at 0° was added slowly a solution of thionyl chloride (12.1 g, 102 mmol) in ethyl acetate (100 mL). After 60 min at 0°, t.l.c. (10:1 toluene–ethanol) revealed only **5** (R_F 0.5). The mixture was filtered, washed twice with saturated aqueous sodium chloride, dried (Na$_2$SO$_4$), and concentrated at 30° (bath) to give the crude cyclic sulphite **5** (38.7 g, 100 mmol, 99%).

A solution of **5** (45.5 g, 119 mmol) in *N,N*-dimethylformamide (600 mL) was stirred with lithium azide (13 g, 267 mmol) at 90°. After 8 h, t.l.c. (5:1 toluene–ethyl acetate) revealed only **6** (R_F 0.9), and 75% of the solvent was evaporated under a high vacuum at 30° (bath). A solution of the residue in ethyl acetate (400 mL) was washed twice with saturated aqueous sodium chloride, dried (Na$_2$SO$_4$), and concentrated. Column chromatography of the crude product (10:1 toluene–ethyl acetate) on silica gel (500 g) gave **6** (22.4 g, 62 mmol, 52%), isolated as a syrup, $[\alpha]_D^{20}$ −1.2° (*c* 1, chloroform).

Anal. Calc. for $C_{17}H_{22}N_4O_5$: C, 56.4; H, 6.1; N, 15.5. Found: C, 55.6; H, 6.3; N, 15.1.

The 3-acetate had $[\alpha]_D^{20}$ −15° (*c* 0.5, chloroform). ^{1}H-N.m.r. data (CDCl$_3$): δ 1.36, 1.44, 2.12 (3 s, 9 H, 3 CMe), 2.89 (dd, 1 H, $J_{1a,1e}$ 13.9, $J_{1a,2}$ 10.3 Hz, H-1*a*), 3.15 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{5,6a}$ 6.1, $J_{5,6b}$ 16.1 Hz, H-5), 3.52 (ddd, 1 H, $J_{1e,2}$ 4.6, $J_{2,3}$ 8.7 Hz, H-2), 3.76 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-4), 4.22 (dd, 1 H, H-1*e*), 4.31–4.42 (m, 2 H, H-6a,6b), 4.94 (dd, 1 H, H-3), 5.11 (2 d, 2 H, J_{AB} 12.2 Hz, PhC*H*$_2$).

*3-Azido-*N*-benzyloxycarbonyl-1,2,5-trideoxy-1,5-imino-4,6-*O*-isopropylidene-*D*-altritol* (**7**). — This compound (1.8 g, 5 mmol, 8%) was eluted after **6** above and had $[\alpha]_D^{20}$ −37° (*c* 1, chloroform).

Anal. Calc. for $C_{17}H_{22}N_4O_5$: C, 56.4; H, 6.1; N, 15.5. Found: C, 56.9; H, 5.9; N, 15.7.

The 2-acetate had the following ^{1}H-n.m.r. data (CDCl$_3$): δ 1.44, 1.54, 1.72 (3 s, 9 H, 3 CMe), 3.14 (dd, 1 H, $J_{1a,1e}$ 15.0, $J_{1a,2}$ 1.5 Hz, H-1*a*), 3.54 (ddd, 1 H, $J_{4,5}$ 10.7, $J_{5,6a}$ 5.1, $J_{5,6b}$ 10.7 Hz, H-5), 3.85 (bdd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 3.5 Hz, H-3), 4.18 (dd, 1 H, H-4), 4.20 (ddd, 1 H, $J_{1e,2}$ 1.2 Hz, H-1*e*), 4.31 (dd, 1 H, $J_{6a,6b}$ 11.9 Hz, H-6a), 4.70 (dd, 1 H, H-6b), 4.75 (bddd, 1 H, H-2), 5.01–5.12 (2 d, 2 H, J_{AB} 12.4 Hz, PhC*H*$_2$), 7.25–7.41 (m, 5 H, Ph).

*2-Azido-3-*O*-benzyl-*N*-benzyloxycarbonyl-1,2,5-trideoxy-1,5-imino-4,6-*O*-isopropylidene-*D*-glucitol* (**8**). — To a solution of **7** (44.2 g, 122 mmol) in anhydrous tetrahydrofuran (500 mL) in which powderised potassium hydroxide (20.5 g, 365 mmol) was suspended, benzyl bromide (23 g, 135 mmol) was added. After 8 h at 60° under sonication, t.l.c. (20:1 toluene–acetone) revealed only **8** (R_F 0.2). The solids were removed, the solvent was evaporated, and the residue was subjected to column chromatography (toluene→40:1 toluene–acetone) on silica gel (250 g) to give **8** (44.7 g, 99 mmol, 81%), $[\alpha]_D^{20}$ −15° (*c* 0.5, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.43, 1.49 (2 s, 6 H, CMe_2), 2.69 (dd, 1 H, $J_{1a,1e}$ 13.7, $J_{1a,2}$ 10.4 Hz, H-1*a*), 3.07 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{5,6a}$ 5.0, $J_{5,6b}$ 10.7 Hz, H-5), 3.41 (dd, 1 H, $J_{2,3} = J_{3,4} = 8.5$ Hz, H-3), 3.48 (ddd, 1 H, $J_{1e,2}$ 4.8 Hz, H-2), 3.83 (dd, 1 H, H-4), 4.17 (dd, 1 H, H-1*e*), 4.28 (dd, 1 H, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.46 (dd, 1 H, H-6b), 4.73–4.89 (2 d, 2 H, J_{AB} 11.0 Hz, PhCH_2), 5.03–5.13 (2 d, 2 H, J_{AB} 12.2 Hz, PhCH_2).

Anal. Calc. for $C_{24}H_{28}N_4O_5$: C, 63.7; H, 6.2; N, 12.4. Found: C, 64.2; H, 6.6; N, 12.1.

*2-Azido-3-*O*-benzyl-*N*-benzyloxycarbonyl-1,2,5-trideoxy-1,5-imino-*D*-glucitol* (**9**). — To a solution of **8** (44.7 g, 99 mmol) in aqueous 50% acetic acid (500 mL) containing 10% of dichloromethane, conc. hydrochloric acid was added to pH 3. After 90 min at 60°, t.l.c. (1:1 toluene–ethyl acetate) revealed only **9** (R_F 0.3). Sodium hydrogencarbonate was added to pH 4.5, the solvent was evaporated, and the residue was partitioned in 1:1 $CHCl_3$–H_2O (200 mL). The aqueous phase was extracted again with chloroform, and the combined organic phases were dried (Na_2SO_4) and concentrated, to give **9** (38 g, 92 mmol, 98%), $[\alpha]_D^{20}$ +32° (*c* 1, chloroform).

Anal. Calc. for $C_{21}H_{24}N_4O_5$: C, 61.2; H, 5.9; N, 13.6. Found: C, 59.3; H, 5.3; N, 13.9.

*2-Azido-3-*O*-benzyl-*N*,6-*O*-carbonyl-1,2,5-trideoxy-1,5-imino-*D*-glucitol* (**10**). — A solution of **9** (41 g, 99 mmol) in 9:1 *N,N*-dimethylformamide–H_2O (200 mL) was stirred with potassium carbonate (27.6 g, 200 mmol) at 60°. After 8 h, t.l.c. (1:3 hexane–ethyl acetate) showed that the reaction was complete. The mixture was filtered, the solvent was evaporated, and a solution of the residue in ethyl acetate was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated to give **10** (24.7 g, 81 mmol, 82%), m.p. 110°, $[\alpha]_D^{20}$ −27° (*c* 0.5, chloroform). Mass spectrum: *m/z* 322 ($M^+ + 1 + NH_3$).

Anal. Calc. for $C_{14}H_{16}N_4O_4$: C, 55.3; H, 5.3; N, 18.4. Found: C, 54.1; H, 5.6; N, 18.7.

The 4-acetate had the following ^{1}H-n.m.r. data ($CDCl_3$): δ 1.98 (s, 3 H, CMe), 2.70 (dd, 1 H, $J_{1a,1e}$ 13.4, $J_{1e,2}$ 11.0 Hz, H-1*e*), 3.48 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 3.55–3.67 (m, 2 H, H-2,5), 4.09 (dd, 1 H, $J_{1a,2}$ 5.6 Hz, H-1*a*), 4.22 (dd, 1 H, $J_{6a,6b}$ 9.1, $J_{6a,5}$ 4.8 Hz, H-6a), 4.32 (dd, 1 H, $J_{6b,5}$ 7.9 Hz, H-6b), 4.69, 4.89 (2 d, 2 H, J_{AB} 11.1 Hz, PhCH_2), 4.92 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4).

*2-Azido-3-*O*-benzyl-*N*,6-*O*-carbonyl-1,2,5-trideoxy-1,5-imino-4-*O*-methanesulfonyl-*D*-glucitol* (**11**). — To a solution of **10** (22.7 g, 75 mmol) in acetone (250 mL) at 0° was added triethylamine (22.8 g, 225 mmol), and then a solution of mesyl chloride (14.2 g, 125 mmol) in acetone (50 mL) was added slowly. After 30 min, t.l.c. (2:1 ethyl acetate–hexane) revealed only **11** (R_F 0.4). The precipitated salts were removed, the solvent was evaporated, and a solution of the residue in ethyl acetate was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated to give **11** (23.2 g, 61 mmol, 81%), m.p. 173°, $[\alpha]_D^{20}$ +15° (*c* 0.9, chloroform). Mass spectrum: *m/z* 400 (M^+

+ 1 + NH_3). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.76 (dd, 1 H, $J_{1a,1e}$ 13.7, $J_{1a,2}$ 11.0 Hz, H-1*a*), 2.82 (s, 3 H, CMe), 3.52 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 3.60 (dd, 1 H, $J_{1e,2}$ 5.4 Hz, H-2), 3.79 (ddd, $J_{4,5}$ 9.3, $J_{5,6a}$ 7.8, $J_{5,6b}$ 4.8 Hz, H-5), 4.14 (dd, 1 H, H-1*e*), 4.39 (dd, 1 H, H-4), 4.42 (dd, 1 H, $J_{6a,6b}$ 9.7 Hz, H-6a), 4.56 (dd, 1 H, H-6b), 4.73, 5.04 (2 d, 2 H, J_{AB} 10.9 Hz, PhC*H*$_2$).

Anal. Calc. for $C_{15}H_{18}N_4O_6S$: C, 47.1; H, 4.7; N, 14.6. Found: C, 46.8; H, 4.9; N, 14.1.

*2-Azido-4-*O*-benzoyl-3-*O*-benzyl-*N*,6-*O*-carbonyl-1,2,5-trideoxy-1,5-imino-*D*-galactitol* (**12**). — A mixture of **11** (21.2 g, 52 mmol), anhydrous *N,N*-dimethylformamide (350 mL), and lithium benzoate (8.0 g, 62 mmol) was stirred for 72 h at 100°. T.l.c. (2:1 ethyl acetate–hexane) then revealed only **12** (R_F 0.30). The solvent was evaporated, the residue was extracted several times with hot ethyl acetate, and the combined eluates were concentrated to give **12** (20 g, 49 mmol, 94%), m.p. 161°, $[\alpha]_D^{20}$ +112° (*c* 0.4, chloroform); ν_{max} 2115 (N_3), 1774 and 1713 cm^{-1} (C=O) (KBr). Mass spectrum: *m/z* 426 (M^+ + 1 + NH_3). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.73 (dd, 1 H, $J_{1a,1e}$ 13.8, $J_{1a,2}$ 11.3 Hz, H-1*a*), 3.58 (dd, 1 H, $J_{2,3}$ 9.3, $J_{3,4}$ 2.5 Hz, H-3), 3.91 (ddd, 1 H, $J_{1e,2}$ 6.2 Hz, H-2), 3.96 (ddd, 1 H, $J_{4,5}$ 2.0, $J_{5,6a}$ 3.2, $J_{5,6b}$ 8.9 Hz, H-5), 4.1 (dd, 1 H, $J_{6a,6b}$ 9.2 Hz, H-6a), 4.23 (dd, 1 H, H-1*e*), 4.38 (dd, 1 H, H-6b), 4.59, 4.84 (2 d, 2 H, J_{AB} 11.4 Hz, PhC*H*$_2$), and 7.2–8.1 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{21}H_{20}N_4O_5$: C, 61.8; H, 4.9; N, 13.7. Found: C, 62.3; H, 4.4; N, 13.4.

*2-Azido-3-*O*-benzyl-*N*,6-*O*-carbonyl-1,2,5-trideoxy-1,5-imino-*D*-galactitol* (**13**). — To a solution of **12** (20 g, 49 mmol) in 10:1 methanol–CH_2Cl_2 (150 mL) was added 10M sodium hydroxide (5 mL), and the mixture was kept at 40°. After 8 h, t.l.c. (2:1 ethyl acetate–hexane) revealed only **12** (R_F 0.15). The mixture was neutralized with M hydrochloric acid and the solvent was evaporated. The residue was partitioned in 1:1 $CHCl_3$–H_2O, and the organic phase was dried (Na_2SO_4) and then concentrated. The residue crystallized on storage to give **13** (14.0 g, 46 mmol, 94%), m.p. 159°, $[\alpha]_D^{20}$ −16° (*c* 0.7, chloroform); ν_{max} 2120 (N_3), 1747 cm^{-1} (C=O) (KBr). Mass spectrum: *m/z* 305 (M^+ + 1).

Anal. Calc. for $C_{14}H_{16}N_4O_4$: C, 55.3; H, 5.3; N, 18.4. Found: C, 55.9; H, 5.3; N, 18.8.

The 4-acetate had the following ^{1}H-n.m.r. data ($CDCl_3$): δ 2.13 (s, 3 H, CMe), 2.63 (dd, 1 H, $J_{1a,1e}$ 13.8, $J_{1a,2}$ 11.2 Hz, H-1*a*), 3.45 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 2.8 Hz, H-3), 3.74–3.85 (m, 2 H, H-2,5), 3.99 (dd, 1 H, $J_{5,6a}$ 3.8, $J_{6a,6b}$ 9.2 Hz, H-6a), 4.10 (dd, 1 H, $J_{1e,2}$ 6.2 Hz, H-1*e*), 4.30 (dd, 1 H, $J_{5,6b}$ 8.8 Hz, H-6b), 4.52 (d, 1 H, J_{AB} 11.2 Hz, C*H*$_2$Ph), 4.71 (d, 1 H, C*H*$_2$Ph), 5.49 (dd, 1 H, $J_{4,5}$ 2.3 Hz, H-4), and 7.3–7.4 (m, 5 H, Ph).

*2-Azido-3-*O*-benzyl-1,2,5-trideoxy-1,5-imino-*D*-galactitol* (**14**). — To a solution of **13** (8.05 g, 28.9 mmol) in 4:1 methanol–H_2O (150 mL) was added $Ba(OH)_2 \cdot 8H_2O$ (68.3 g, 216 mmol). The mixture was heated to reflux for 8 h, when t.l.c. (3:1 toluene–ethanol) revealed only **14** (R_F 0.15). The barium salts, precipitated by the addition of solid CO_2, were centrifuged, resuspended in methanol, and centrifuged several more times. The combined supernatant solutions were concentrated to dryness, to give **13** (6.4

g, 22.8 mmol, 79%), $[a]_D^{20}$ +2°(c 1, chloroform). ^{1}H-N.m.r. data (CD_3OD): δ 2.31 (dd, 1 H, $J_{1a,1e}$ 12.6, $J_{1a,2}$ 11.2 Hz, H-1a), 2.58 (ddd, 1 H, $J_{4,5}$ 1.1, $J_{5,6a} = J_{5,6b} = 6.6$ Hz, H-5), 3.11 (dd, 1 H, $J_{1e,2}$ 5.5 Hz, H-1e), 3.35 (dd, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 2.9 Hz, H-3), 6.9 (d, 2 H, H-6a,6b), 3.75 (ddd, 1 H, H-2), 4.19 (dd, 1 H, H-4), 4.60, 4.78 (2 d, 2 H, J_{AB} 11.6 Hz, PhCH_2), and 7.2–7.5 (m, 5 H, Ph).

Anal. Calc. for $C_{13}H_{18}N_4O_3$: C, 56.1; H, 6.5; N, 20.1. Found: C, 55.4; H, 6.1; N, 19.8.

*2-Acetamido-1,2,5-trideoxy-1,5-imino-*D*-galactitol* (**1**). — A solution of **14** (2.78 g, 10 mmol) in acetic anhydride (100 mL) was hydrogenolysed over 10% Pd–C under a hydrogen pressure of 1.5 MPa for 10 h, when t.l.c. (4:3:1 chloroform–methanol–aqueous NH_3) revealed only **1** (R_F 0.31). The mixture was filtered, pyridine (200 mL) was added, and the mixture was kept at 40° for 5 h and then concentrated. A solution of the residue in CH_2Cl_2 was washed with semi-saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated. M.p.l.c. (toluene→10:1 toluene–ethanol) of the residue followed by deacetylation in methanolic sodium methoxide yielded a syrupy product that was freeze-dried from H_2O to give **1** (1.27 g, 6.2 mmol, 62%), $[a]_D^{20}$ +37° (c 1, methanol), R_F 0.31 (4:3:1 chloroform–methanol–aqueous ammonia). Mass spectrum: m/z 205 (M^+ + 1).

Anal. Calc. for $C_8H_{16}N_2O_4$: C, 47.0; H, 7.9; N, 13.7. Found: C, 46.8; H, 8.0; N, 13.6.

The hydrochloride of **1** had the following ^{1}H-n.m.r. data (D_2O): δ 1.91 (s, 3 H, CMe), 2.79 (dd, 1 H, $J_{1a,1e}$ 12.5, $J_{1a,2}$ 12.0 Hz, H-1a), 3.28–3.41 (m, 2 H, H-1e,5), 3.6–3.8 (m, 3 H), 4.08 (bs, 1 H, H-4), 4.2 (ddd, 1 H, H-2).

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